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**Patentanmeldung Nr. | Patent application No. | Demande de brevet n°**

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

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Anmelder/Applicant(s)/Demandeur(s):

Nederlandse Organisatie voor toegepast-
natuurwetenschappelijk Onderzoek TNO
Schoemakerstraat 97
2628 VK Delft
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Use of protein hydrolysate derived from keratin-containing material as a paper product additive

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Title: USE OF PROTEIN HYDROLYSATE DERIVED FROM KERATIN-CONTAINING MATERIAL AS A PAPER PRODUCT ADDITIVE

The present invention relates to the use of protein hydrolysate derived from keratin-containing material as a paper product additive, and paper pulp and paper products comprising such a protein hydrolysate additive.

In the papermaking industry a wide variety of additives is applied to improve properties of the finished paper product. Such properties include, for instance, printability, wet/dry strength, softness and wetting properties. Generally, the amounts of additives to be used need to be carefully controlled because most of these additives are expensive chemicals.

Object of the present invention is to provide a new class of cheap additives which can attractively be used in the production of paper products.

Surprisingly, it has now been found that protein hydrolysate derived from keratin-containing material can attractively be used as a paper product additive.

Accordingly, the present invention relates to the use of a protein hydrolysate derived from keratin-containing material as an additive in a paper product.

The present invention enables the production of very high quality paper products in a very cost-effective manner. The paper products obtained in accordance with the present invention display excellent quality properties in terms of strength and volume per mass.

The protein hydrolysate to be used in accordance with the present invention can be derived from a wide variety of keratin-containing materials. The keratin-containing materials can suitably be derived from mammals and/or birds. Suitable keratin-containing materials from which the protein hydrolysate can be derived include mammalian hair, animal hooves, claws, horns, and feathers. The protein hydrolysate is preferably derived from mammalian hair and/or feathers. More preferably, the protein hydrolysate is

derived from mammalian hair, in particular from livestock, and more particularly from pigs and chicken feathers.

The protein hydrolysate to be used in accordance with the present invention can suitable be prepared by subjecting the keratin-containing material to an oxidation treatment in which the keratin-containing material is contacted with a solution which comprises a bleaching agent. The solution to be used in the oxidation treatment has been made alkaline (above pH 7) or acidic (below pH 7). Preferably, the solution has been made alkaline by the addition of NaOH, KOH and/or $NH_4OH$ or acidic by the addition of one or more (organic) acid(s). A wide variety of (organic) acids can be used, including acetic acid and formic acid.

The pH value of the alkaline solution to be used in step (a) is preferably in the range of from 9-13, more preferably in the range of from 10-12. The pH value of the acidic solution is preferably in the range of from 3-7, more preferably in the range of from 4-6.

Suitable bleaching agents include organic and inorganic peroxides. Preferably, use is made of a bleaching agent selected from the group of hypohalides, perborates, percarbonates, organic peroxides, or hydrogen peroxide. More preferably, the bleaching agent comprises hydrogen peroxide. One single bleaching agent or a mixture of bleaching agents can suitably be applied in the alkaline or acidic solution. In the alkaline solution preferably inorganic peroxides are used, whereas in the acidic solution preferably organic peroxides are used. Suitably, the bleaching agent is used in an amount in the range of from 0.1% (w/w) to 40% (w/w), preferably in the range of from 0.3% (w/w) to 30% (w/w), based on total alkaline or acidic solution.

In the oxidation treatment the keratin-containing material can suitably be contacted with the alkaline or acidic solution over a period of time in the range of from 5 minutes to 16 hours, preferably in the range of from 15 minutes to 10 hours. The temperature to be applied in the oxidation treatment

can suitably be in the range of from room temperature to 100°C, preferably in the range of from 30°C to 80°C.

The keratin-containing material can be one type of keratin-containing material or it can be a mixture of different types of keratin-containing materials.

The keratin-containing material to be subjected to the oxidation treatment is preferably first subjected to a washing step in which soluble components, such as for instance blood, urine remnants and other animal components, are removed from the keratin-containing material before the keratin-containing material is subjected to the oxidation step.

The protein hydrolysate obtained in the oxidation treatment and contained in the solution can subsequently be recovered by separating it from the remaining keratin-containing material. This can be established by means of known techniques. For this purpose use can, for instance, be made of a conventional filtering system. In this way a solution of the protein hydrolysate can be obtained. In order to recover the protein hydrolysate from the protein hydrolysate solution so obtained, the pH value of the solution can suitably be adjusted so as to allow the protein hydrolysate to precipitate, after which the protein hydrolysate precipitate can be recovered by methods known per se. The pH of the solution is preferably adjusted so as to be in the range of from 1 to 5, more preferably to be in the range of 2 to 4. The pH adjustment can be established by adding in a controlled manner, for instance by way of titration, an organic and/or inorganic acid to the solution. Suitable acids include hydrochloric acid, sulphuric acid, acetic and formic acid, and the like.

Suitably, the pH adjustment can be carried out over a period of time in the range of from 5 minutes to 10 hours, preferably in the range of from 20 minutes to 8 hours The temperature to be applied during the pH adjustment can suitably be in the range of from 15°C to 100°C, preferably in the range of from 25°C to 70°C.

Suitably, the protein hydrolysate precipitate obtained can be dissolved in a liquid medium to obtain a solution which can be used as a paper product additive. Such a liquid medium suitably includes virgin and/or recycled cellulose fibres and/or known additives used in the wet-end of the paper process. Preferably, water or recycled water is used as the liquid medium. To the protein hydrolysate solution so obtained one or more other paper product additives can be added before the solution is used to produce a paper product. These other additives may contribute to different properties of the paper product to be obtained. The concentration of the protein hydrolysate will suitably be in the range of from 0.1% (w/w) to 50% (w/w), based on total fibre weight. Preferably, the concentration of the protein hydrolysate is in the range of from 0.3% (w/w) to 40% (w/w), based on total fibre weight.

Alternatively, the protein hydrolysate precipitate can as such be added to a solution containing one or more other additives to be used in the manufacturing of a paper product. In another suitable embodiment the protein hydrolysate precipitate is added directly to the paper pulp where after it is thoroughly mixed with other paper pulp components.

Preferably, the protein hydrolysate additive is used in the form of a solution.

The protein hydrolysate additive can be added at one or more different stages of the paper production process. The protein hydrolysate additive can also suitably be added to the paper product after the latter has been prepared.

In the context of the present invention the term "paper product" is meant to include all sorts of papers, such as printing paper, tissue/hygiene, newspaper, office paper, specialties, but also materials such as cardboard, folding board, box board, undulated board, corrugated board, and 3D board and the like.

The present invention also relates to paper pulp comprising protein hydrolysate derived from keratin-containing material. Suitably, such paper pulp comprises protein hydrolysate derived from keratin-containing material

in an amount in the range of from of from 0.1 to 50 wt.%, based on total paper pulp. Preferably, such paper pulp comprises protein hydrolysate derived from keratin-containing material in an amount in the range of from 0.3 to 40 wt.%, based on total paper pulp.

Further, the present invention also relates to a paper product comprising protein hydrolysate derived from keratin-containing material. Suitably, such paper product comprises protein hydrolysate derived from keratin-containing material in an amount in the range of from 0.1 to 50 wt.%, based on total paper product. Preferably, such paper product comprises protein hydrolysate derived from keratin-containing material in an amount in the range of from 0.3 to 40 wt.%, based on total paper product.

Examples

Preparation of protein hydrolysate.

To a mixture of 250 grams of hair was added 9 litres of water and subsequently the pH of the mixture was brought to a level suitable for bleaching. Then the temperature of the mixture was raised to 65 – 70°C and 200 ml of a 30% (w/w) solution of hydrogen peroxide (pH 11) or 60 ml of a 32% (w/w) of peracetic acid (pH 5) was added. The mixture was then stirred for 16 hours after which the hydrolysate was isolated by lowering the pH of the reaction mixture to 3. Once the precipitate was formed it was collected through filtration and dried at 70°C. After drying, the obtained product may optionally be grinded into a powder.

Evaluation of the protein hydrolysate

The hydrolysate (0, 1, 5, 10, 15% (w/w)) was mixed with virgin cellulose fibrers from Eucalyptus in such a way that for each mixture a constant weight of

cellulose fibrers was obtained. Also sheets were using only the virgin Eucalyptus cellulose fibrers for comparison and evaluation results are depicted as 0% (w/w). The sheets were obtained by using a FRET (Formation and Retention Tester), using a vacuum of 0.5 bar. The sheets were dried at 100°C, using a Rapid Köthen drying cell. For each mixture three sheets were made.

From each mixture the paper properties were determined

Volume per mass ($cm^3$/gram):

The volume per mass was calculated by dividing the thickness of the sheet by weight per $m^2$. Table 1 gives the results of the different sheets

The volume per mass was reduced with increase of % protein hydrolysate. It seems that the protein hydrolysate was able to fill the pores formed by the cellulose fibre web.

Table 1: Volume per mass of sheets

| %Hydrolysate added (w/w) | Volume per mass ($cm^3$/g) |
|---|---|
| 0 | 1.55 |
| 1 | 1.53 |
| 5 | 1.49 |
| 10 | 1.46 |
| 15 | 1.47 |

Porosity:

The effect of the addition of protein hydrolysate is depicted in Figure 1.

With increase of the % added protein hydrolysate the porosity of the sheets decreased. The effect is clearly visible starting from 5% (w/w) added protein hydrolysate.

Short compression test:

The influence of protein hydrolysate as additive in cellulose pulp on the SCT index is depicted in Figure 2. The added protein hydrolysate has a positive influence on the short compression test index.

Z-directional tensile:

The influence of protein hydrolysate on the Z-directional tensile is depicted in Figure 3. Figure 3 shows that increased addition of protein hydrolysate in cellulose fibre has a positive influence on the fibre interaction.

Tensile index:

This parameter is measured to evaluate the force at break and gives an indication of the length of the paper needed before it breaks. Figure 4 shows the results when part of the cellulose fibre is replaced by protein hydrolysate. There is a sharp increase on the length of break with increased weight percent of protein hydrolysate implying a stronger paper. This effect coincides with earlier observed improved fibre-fibre interaction.

Stretch at break:

This parameter gives an indication of the amount of stretch of the paper sheet before it breaks. The results are depicted in Figure 5. The results fit well within the earlier results presented in Figures 3 and 4. An increase in weight of protein hydrolysate also gives an increase in stretch at break.

## Claims

1. Use of a protein hydrolysate derived from keratin-containing material as an additive in a paper product.

2. Use according to claim 1, wherein the protein hydrolysate is derived from mammalian hair and/or feathers.

3. Use according to claim 2, wherein the protein hydrolysate is derived from mammalian hair.

4. Use according to claim 2, wherein the protein hydrolysate is derived from feather

5. Use according to claim 3, wherein the mammalian hair is derived from livestock.

6. Use according to claim 4, wherein the feather is derived from chicken

7. Use according to claim 5, wherein the mammalian hair is derived from pigs.

8. Paper pulp comprising protein hydrolysate derived from keratin-containing material.

9. Paper pulp according to claim 8, comprising protein hydrolysate derived from keratin-containing material in an amount of from 0.1 to 50 wt.%, based on total paper product.

10. Paper pulp according to claim 9, comprising protein hydrolysate derived from keratin-containing material in an amount of from 0.3 to 40 wt.%, based on total paper product.

11. Paper product comprising protein hydrolysate derived from keratin-containing material.

12. Paper product according to claim 11, wherein protein hydrolysate derived from keratin-containing material is present in an amount of from 0.1 to 50 wt.%, based on total paper product.

13. Paper product according to claim 12, wherein protein hydrolysate derived from keratin-containing material is present in an amount of from 0.3 to 40 wt.%, based on total paper product.

Abstract

The invention relates to the use of a protein hydrolysate derived from keratin-containing material as an additive in a paper product. The invention further relates to paper pulp or a paper product comprising protein hydrolysate derived from keratin-containing material.

Figure 1

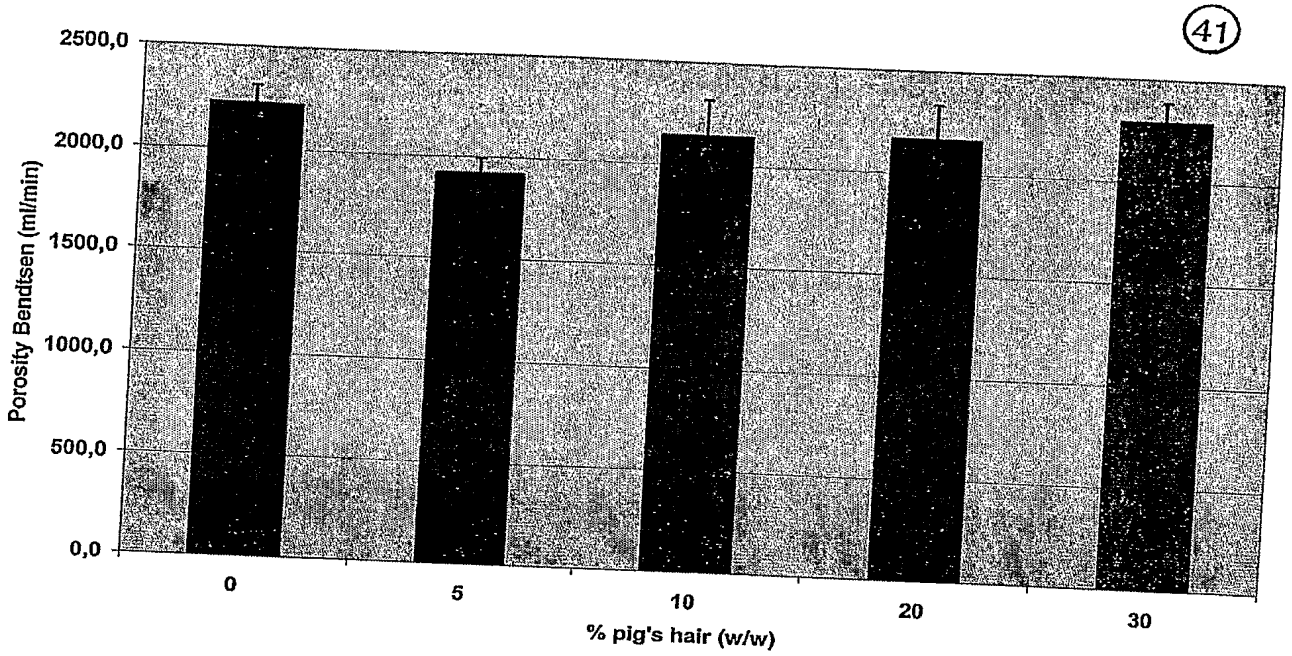

Figure 2

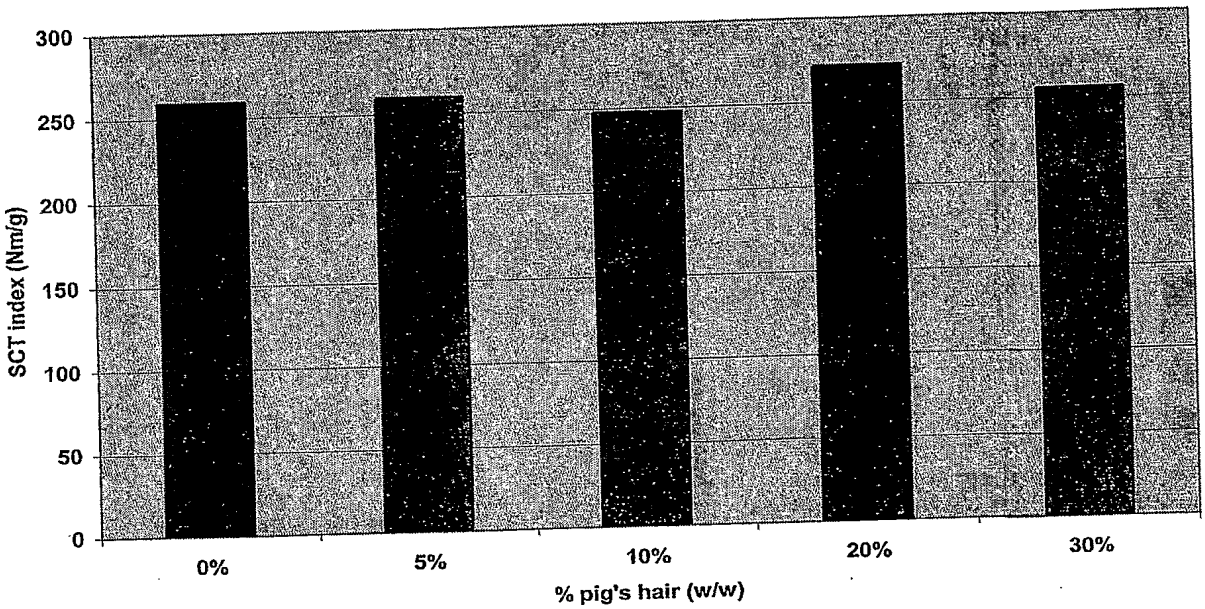

Figure 3

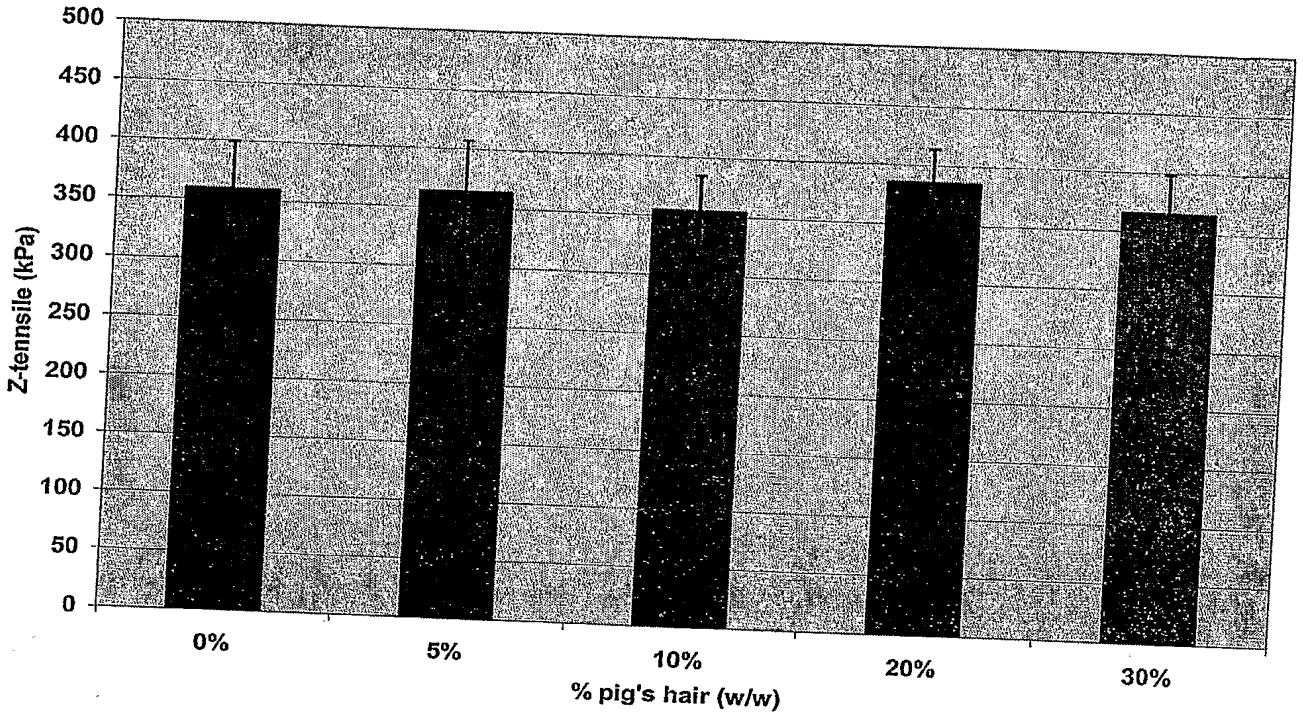
500
450
400
350
300
250
200
150
100
50
0
Z-tennsile (kPa)
0%
5%
10%
20%
30%
% pig's hair (w/w)

Figure 4

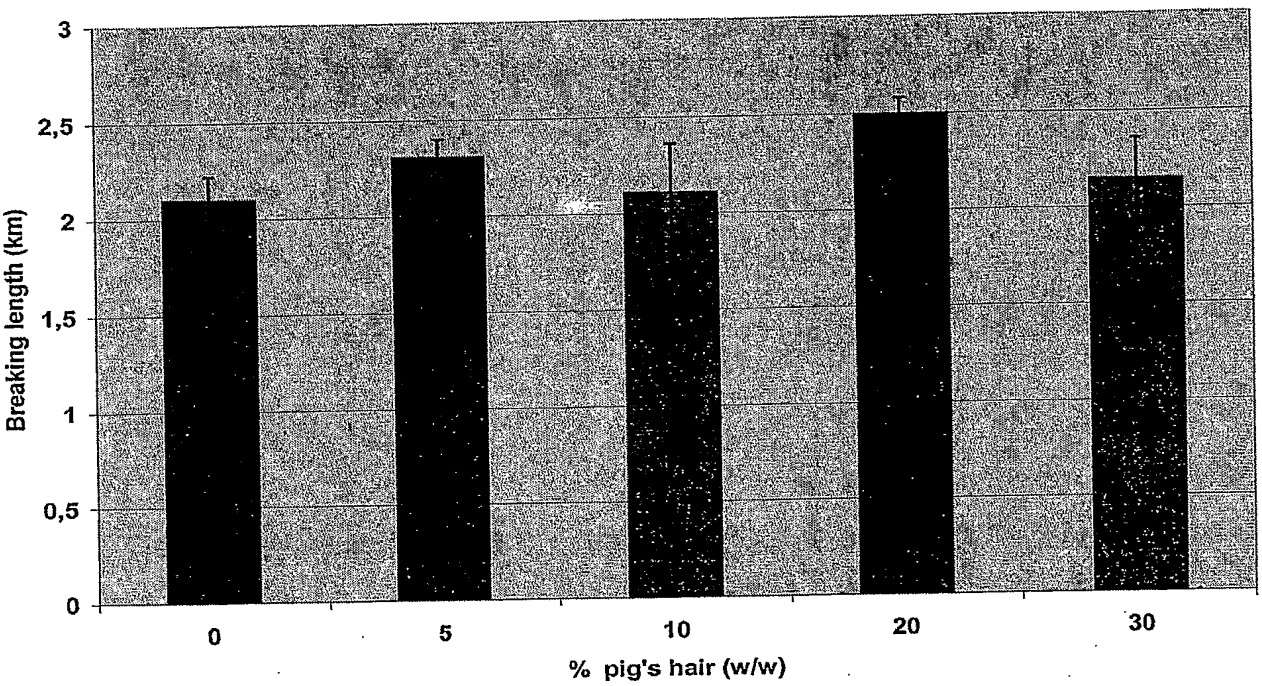

Figure 5